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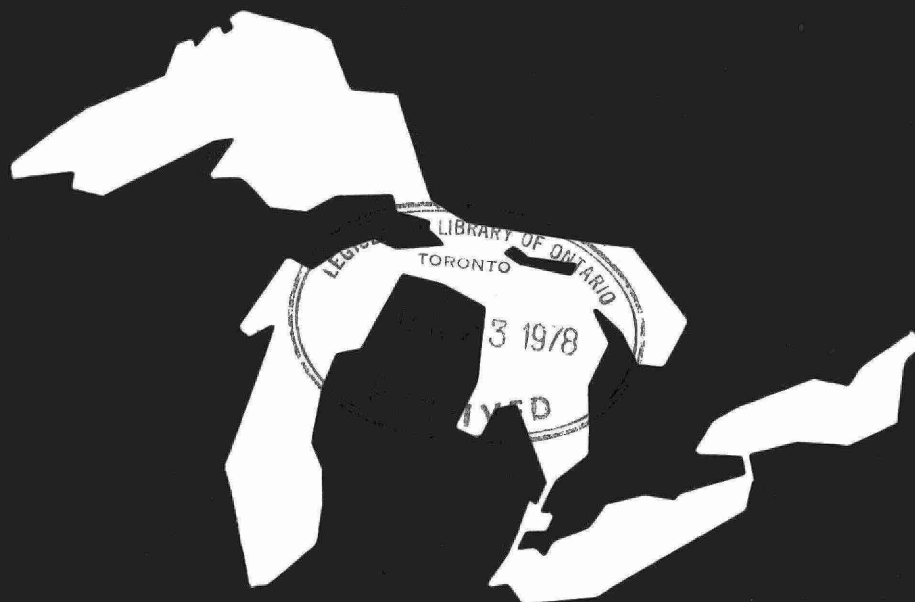
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Reuse of Waste SO_2 and Phosphate Sewage Sludges by Solidification with Lime and Fly Ash

Research Report No. 69



**Research Program for the Abatement of Municipal Pollution
under Provisions of the Canada-Ontario Agreement
on Great Lakes Water Quality**

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REUSE OF WASTE SO₂ AND PHOSPHATE SEWAGE
SLUDGES BY SOLIDIFICATION WITH LIME AND FLY ASH

by

Acres Consulting Services Limited
Niagara Falls, Canada

RESEARCH PROGRAM FOR THE ABATEMENT
OF MUNICIPAL POLLUTION UNDER THE
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ABSTRACT

The phosphate-bearing sewage sludge disposal problem is becoming more acute each year. Not only are sludge volumes increasing, but disposal methods are becoming more expensive, in part because suitable landfill sites within easy hauling distance are being exhausted. These landfilled sludges are difficult to consolidate sufficiently for future use as building lots, thus reducing land use values. New, less expensive ways of disposing of phosphate-bearing sewage sludge are, therefore, urgently required.

The laboratory phase of this research work indicates the feasibility of mixing sewage sludge with certain other waste ingredients to form a self-setting mix which consolidates well and is capable of long term retention of the phosphates in a cementing matrix. The mix ingredients consisted of fly ash and SO_2 sludges from coal burning thermal power plants and spent acids from industrial processes. Hence, several waste disposal problems may be solved simultaneously. The only commercial commodity required for the process is lime which is easily obtainable and relatively inexpensive. The sludge/fly ash mixture can be produced either as a compactible mix or a liquid slurry. The compactible mix is an excellent base material for road and parking lot construction and could supplement rapidly depleting deposits of natural sand and gravel. The liquid slurry could be piped to landfill sites where it should set-up and gain sufficient strength so that these areas could be used as building sites.

The cementing matrix, when mixed with as much as 6% dry phosphate-bearing sewage sludge, will have adequate strength for highly loaded (>450 psi) landfill. Total phosphate leached during 15 days from a variety of compacted mixtures containing sewage sludge never exceeded 0.01% of the phosphate input to the mixtures.

Further laboratory research is required to determine the effect of changing the proportions of the various ingredients on long term strength gains, leaching of phosphates and survival of pathogens.

RÉSUMÉ

Le problème de mise en décharge des boues résiduelles phosphatées s'aggrave d'année en année. Non seulement le volume des boues augmente-t-il, mais leur transport coûte de plus en plus cher en partie à cause de la raréfaction des décharges situées à courte distance. Il est difficile de consolider suffisamment les boues déversées pour permettre de construire ultérieurement sur ces terrains, ce qui en réduit la valeur. Il est donc urgent de mettre au point de nouvelles méthodes de mise en décharge moins coûteuses.

L'étape expérimentale de cette recherche a démontré qu'on peut mélanger les boues avec certains autres déchets pour former un composé auto-épaississant, se solidifiant bien et qui ait la propriété de retenir les phosphates dans une matrice. Le mélange se compose de cendres légères, de boues au SO_2 provenant de centrales thermiques alimentées au charbon et d'acides épuisés de certains procédés industriels. On peut ainsi résoudre simultanément plusieurs problèmes de déchets. Le procédé n'exige l'achat que d'un seul produit, la chaux, facile à obtenir et relativement peu coûteuse. Les boues et les cendres peuvent être mélangées de manière à se prêter à la consolidation, ou encore, pour obtenir une suspension liquide. Le premier mélange constitue un excellent matériau pour la construction de routes et de terrains de stationnement; il pourrait remplacer le sable et le gravier dont les carrières s'épuisent rapidement. On pourrait canaliser le second aux décharges, où sa solidification rendrait le terrain propice à la construction.

Une fois consolidée, une matrice contenant jusqu'à 6 p. 100 de boues phosphatées séchées pourra résister dans les décharges à des pressions très élevées (plus de $31,7 \text{ kg/cm}^2$). La quantité totale de phosphates entraînés par percolation pendant 15 jours à partir de différents mélanges de boues consolidées n'a jamais dépassé 0,01 p. 100 de la quantité initiale mélangée.

D'autres recherches devront se faire en laboratoire pour déterminer les effets d'une variation des proportions des divers ingrédients sur la consolidation à long terme, la percolation des phosphates et la survie des agents pathogènes.

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In September, 1972, Acres Consulting Services Limited was awarded a contract to carry out a research project on the solidification of phosphate-bearing sewage sludge. The project forms part of the research program sponsored jointly by the Government of Canada and the Government of the Province of Ontario under the Canada-Ontario Agreement on Great Lakes Water Quality.

The objectives of this project were to determine if phosphate can be held in an inert form within a cementing matrix of fly ash, lime, industrial waste sulphuric acid, and sewage sludge, and if the resultant material would have adequate strength to serve as a load-bearing fill.

This report summarizes the work done at Acres laboratory to accomplish these objectives.

CONCLUSIONS

- It is possible to produce a cementing matrix which is composed essentially of waste materials.
- This matrix, when mixed with as much as 6% dry phosphate-bearing sewage sludge, will keep the phosphates in an inert form. The resultant material will have adequate strength for highly loaded (>450 psi) landfill.
Where the resultant material is to be used as lightly loaded landfill (<150 psi), a greater quantity of dry phosphate-bearing sewage sludge can be contained within the cementing matrix than for highly loaded landfill.
- Total phosphate leached during 15 days from a variety of compacted mixtures containing sewage sludge never exceeded 0.01% of the phosphate input to the mixture.

MATERIALS

The following materials were used:

- (a) Fly ash (dry) - Ontario Hydro's Lakeview plant. Sieve analysis is shown in Figure 1, and chemical analyses are given in Tables 1 and 2.
- (b) Sulphur dioxide sludge (wet) - Ontario Hydro's pilot plant at Lakeview. Chemical analyses are shown in Tables 1 and 3.
- (c) Spent sulphuric acid liquor - Stelco, Hamilton, Ontario. Chemical analyses are presented in Tables 1 and 4.
- (d) Hydrated lime - A commercial source in Niagara Falls, Ontario. The phosphate content is given in Table 1.
- (e) Phosphate-bearing sewage sludge - An operating plant at Newmarket, Ontario, by arrangement with the Wastewater Technology Centre, Burlington, Ontario. The phosphate content is given in Table 1.

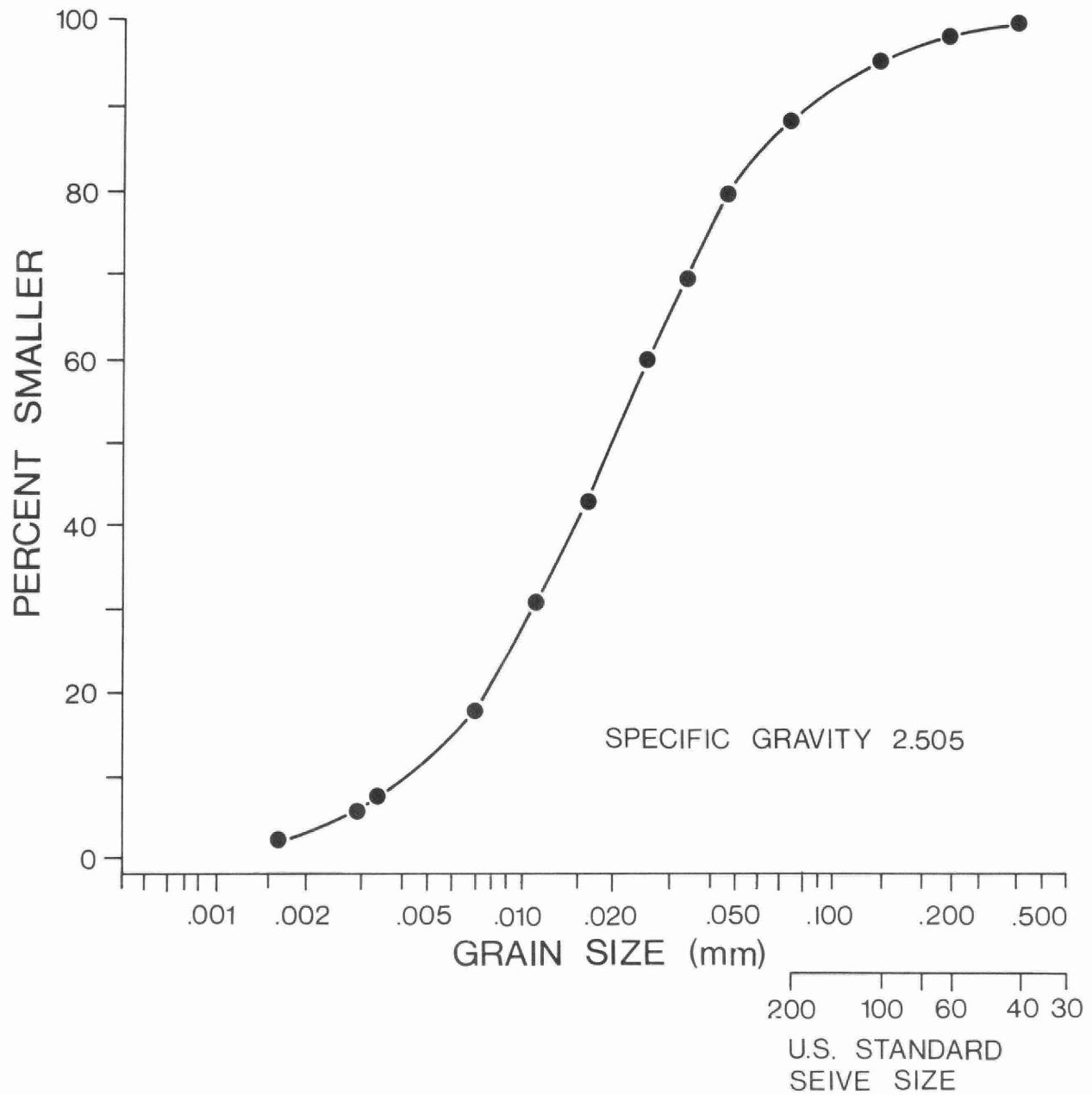


FIG. 1: FLY ASH GRAIN SIZE DISTRIBUTION

TABLE 1. PHOSPHATE CONTENT OF INGREDIENT MATERIALS (DRY WEIGHT BASIS)

Material	Phosphate - mg/gram	
	Soluble	Total
Fly Ash	Trace	1.770
SO ₂ Sludge	Trace	0.287
Spent Acid	Trace	0.004
Neutralized Spent Acid	Trace	0.075
Hydrated Lime	Nil	Trace
Phosphate Sewage Sludge	0.0266	31.000

TABLE 2. CHEMICAL ANALYSIS OF FLY ASH (DRY WEIGHT BASIS)

Constituents	Percent
Moisture (H ₂ O)	1.0
Carbon (C)	6.1
Calcium Oxide (CaO) Combined - Includes Free Lime	5.9
Free Lime (CaO)	0.28
Ferric Oxide (Fe ₂ O ₃)	16.3
Aluminium Oxide (Al ₂ O ₃)	26.7
Magnesium Oxide (MgO)	2.5
Silica (SiO ₂)	40.2
Sulphur (SO ₂)	1.2
Sodium (Na ₂ O)	0.225
Potassium (K ₂ O)	0.19

TABLE 3. CHEMICAL ANALYSIS OF SO₂ SLUDGE

Constituents	Percent
Moisture (H ₂ O)	78.00
Carbon (C)	4.00
Calcium Oxide (CaO)	67.00
Ferric Oxide (Fe ₂ O ₃)	0.56
Aluminium Oxide (Al ₂ O ₃) Dry Weight Basis	0.44
Magnesium Oxide (MgO)	0.80
Silica (SiO ₂)	15.00
Sulphur (SO ₂)	11.30
Sodium (Na ₂ O)	0.0086
Potassium (K ₂ O)	0.0113

TABLE 4. CHEMICAL ANALYSIS OF SPENT ACID
(DRY WEIGHT BASIS)

Constituents	Percent
Iron (Fe)	4.6
Acid (H ₂ SO ₄)	3.4
Total Solids	14.37
Density (g/cc)	1.16

A cementing matrix was developed by mixing fly ash with varying quantities of lime, waste acid and SO_2 sludge. The optimum mix was selected from a comparison of the compressive strengths of test samples. Phosphate-bearing sewage sludge was then added to the selected mix in varying amounts and compressive strength and leaching properties determined. The procedural steps were as follows:

- (a) Lime/fly ash trial mixes were prepared in both the liquid and compacted states. The handling qualities and strength characteristics of the compacted specimens were found to be superior, and, therefore, the compacted state was chosen for the main program.
- (b) The degree of compaction to be utilized in moulding test specimens was determined by means of the standard Proctor compaction test. Compaction tests were conducted on lime/fly ash and lime/fly ash/ SO_2 sludge mixes.
- (c) An accelerated curing apparatus (curing time: four days) was developed for the prediction of 28-day compressive strengths. Four-day compressive strengths were correlated with 28-day results.
- (d) The effects of varying the lime content between 4 and 16% on the compressive strength of lime/fly ash mixtures were determined.
- (e) The effect of the addition of neutralized, spent sulphuric acid to the lime/fly ash mixture was determined.
- (f) The effect of the addition of SO_2 sludge to the lime/fly ash mixture was determined.
- (g) The effect of the addition of neutralized, spent sulphuric acid to the lime/fly ash/ SO_2 sludge mixture was determined.
- (h) A basic matrix, which was the optimum mix with respect to compressive strength from steps (d) to (g), was chosen. This mix contained lime, fly ash, neutralized spent sulphuric acid and SO_2 sludge.

- (i) The effects of the addition of dry phosphate-bearing sewage sludge on the compressive strength and leaching properties of the basic matrix were determined.

5 RESULTS AND DISCUSSION

5.1 Preparation of Mix Specimens for Compressive Strength Tests

Trial mixes were prepared with lime and fly ash in varying proportions in both liquid and compacted states. These were used to assess the relative merits of moulding, handling and testing mixtures at two distinct consistencies.

The compacted mixtures were moulded using a miniature Harvard compaction device. The specimens obtained were 1.31 inches in diameter, 2.82 inches long, and had a volume of 3.81 cubic inches. The compaction force used for moulding the specimens was selected to produce a smooth, well-shaped, extrudable specimen suitable for compressive strength testing. Tests indicated that compressive strengths approaching 1000 pounds per square inch at 28 days could be obtained by this method.

The liquid mixes were moulded using plexiglas tubing to form specimens which were 1.25 inches in diameter and 2.50 inches long. The consistency of each mixture was controlled using a flow cone developed by the U.S. Corps of Engineers, in which 800 cc was required to pass through the flow cone in a period of 55 ± 5 seconds. The moulds were filled in two layers. The material in the mould was tamped after placing each layer to remove any entrapped air. The maximum compressive strength which could be achieved with this method was 200 pounds per square inch at 28 days. The effect of lime content on the compressive strength of a liquid mixture is shown in Figure 2. The specimens produced by this method were difficult to handle, and a great deal of care had to be taken during compressive strength testing in order to obtain reproducible results. For these reasons, it was decided to perform all further tests on compacted mixes.

5.2 Accelerated Curing

An accelerated curing apparatus similar to the one used for the accelerated curing of concrete test specimens was developed in order to shorten the test program. This method enables prediction of the 28-day compressive strength at four days.

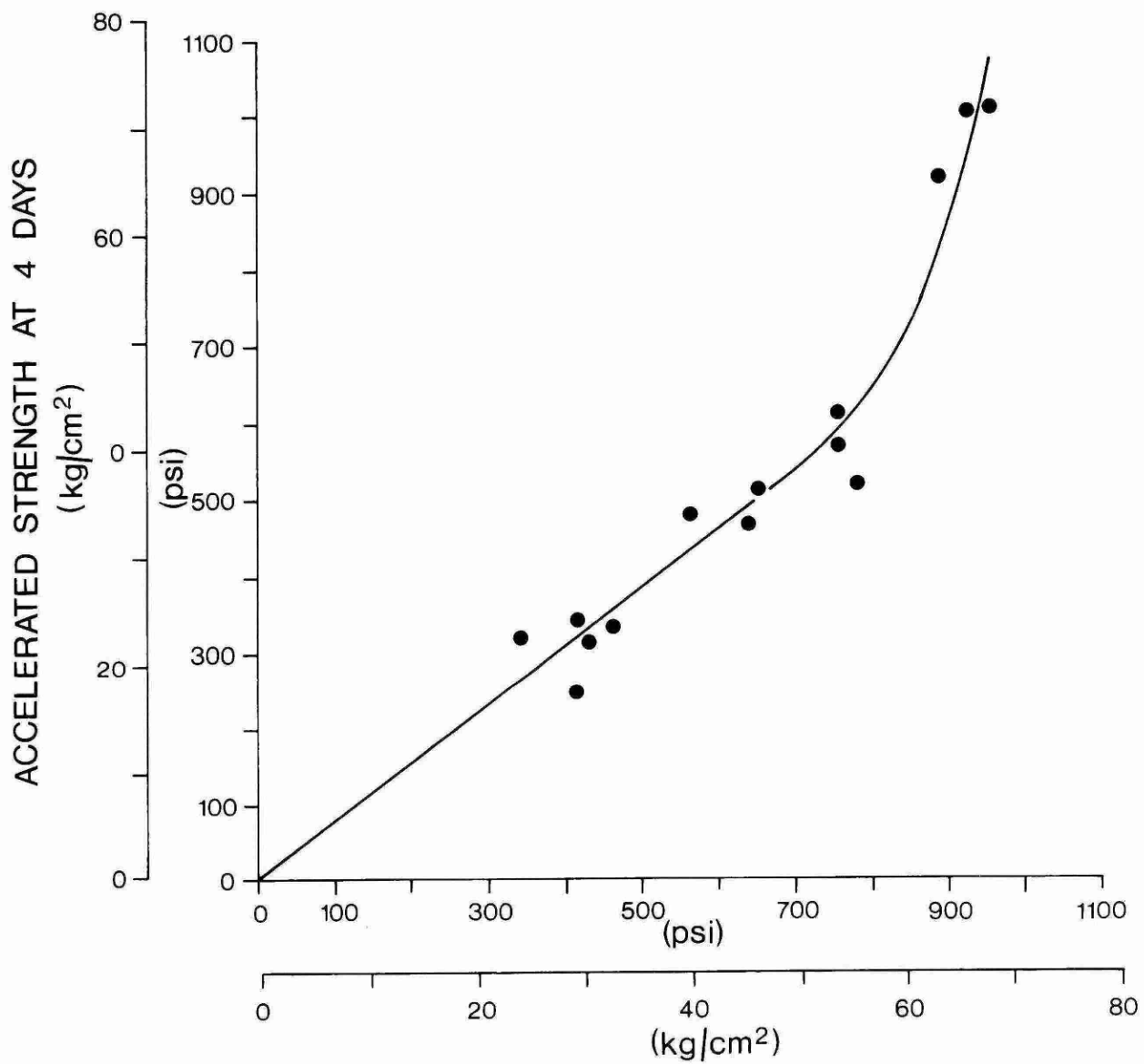


FIG. 2: RELATIONSHIP BETWEEN STANDARD AND
ACCELERATED COMPRESSIVE STRENGTHS

The procedural steps of the accelerated curing cycle were as follows:

- (a) The specimens were cured at 100% humidity and 72°F temperature for the first three days after moulding.
- (b) The specimens were then placed in a curing tank at a temperature of 165°F, 100% humidity at atmospheric pressure.
- (c) After curing 96 hours, the specimens were removed from the accelerated curing tank, allowed to cool for one hour and were tested.

Duplicate specimens were cured for 28 days at the same conditions listed above and then tested. A plot of the four-day versus the 28-day compressive strengths is shown in Figure 2.

Although the curve provides reasonably good prediction of the 28-day strength above 400 pounds per square inch, further work is required to improve the method for lower strengths. This method required skilled handling during compressive strength testing, and the use of very accurate testing equipment. Mix designs were, therefore, chosen at the 450 psi strength level for maximum predictability.

5.3 Development of the Basic Matrix

5.3.1 Basic compacted mix

Standard Proctor compaction tests (Cassell and Walker, 1970) were performed on lime/fly ash mixtures in order to determine the optimum moisture and dry density at which to mould test specimens. The compaction tests were performed in two ways:

- (a) the lime/fly ash material was reused for each run of the test; and
- (b) virgin material was used for each run.

The compaction test results (Figure 3) led to moulding further test specimens at 30.3% moisture and a dry density of 80.7 pounds per cubic foot. A miniature Harvard compaction device was used. Six specimens were moulded from each mixture for compressive strength tests:

- two for accelerated testing at four days;
- two for testing at 28 days; and
- two in reserve for future tests.

Compaction tests were also performed on a lime/fly ash/SO₂ sludge mixture (Figure 4). The results were essentially identical with those for the lime/fly ash mixture.

5.3.2 Effect of lime content

A series of lime/fly ash mixes were tested with the lime varied between 4 and 16% of total solids dry weight. The results of these tests are shown in Figure 5. Both compacted and liquid mixture curves peak at 12 to 14% lime content. This is a good indication that tests on compacted mixtures will be of value in assessing the effect of various combinations of basic materials in liquid mixtures.

A mix with 5% lime was selected. With the Lakeview ash, this would yield a strength of approximately 470 pounds per square inch at 28 days, which is higher than would be required for general fill purposes.

5.3.3 Effect of spent acid waste

A series of mixes was prepared using a constant lime/fly ash mixture (6% lime by weight of total solids) in which a portion of the mix water was replaced with neutralized, spent sulphuric acid waste. The concentration of the acid was 3.4% H₂SO₄. The replacement of mix water by acid was varied from 1 to 40% by weight of total solution. The results (Figure 6), indicated that the compressive strength increased as the concentration of neutralized acid solution was increased.

An additional series of mixtures were tested to check the effect of a constant 20% replacement of mix water by neutralized, spent sulphuric acid liquor on lime/fly ash mixtures, where the lime content was varied as a percentage by weight of total solids. The results (Figure 7) indicated that in the range of lime contents tested, the addition of neutralized spent sulphuric acid waste will increase the compressive strength.

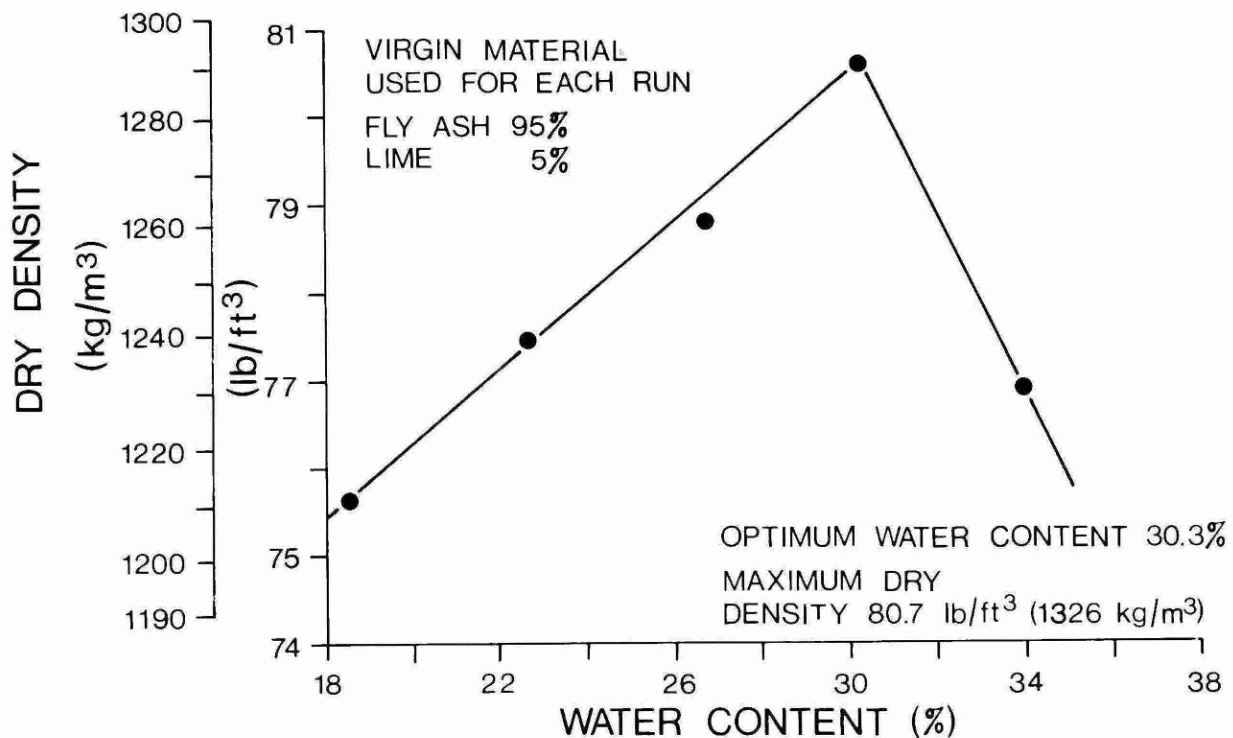
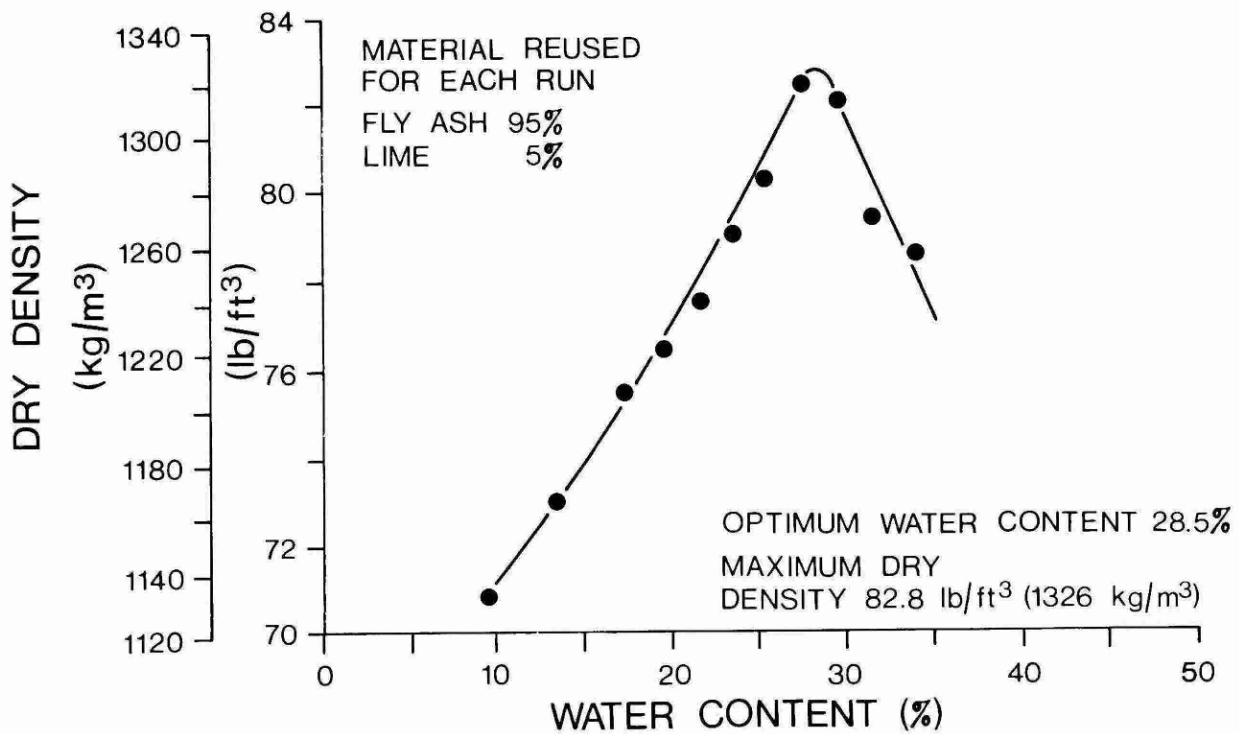


FIG. 3: STANDARD PROCTOR COMPACTION TEST ON A LIME/FLY ASH MIXTURE

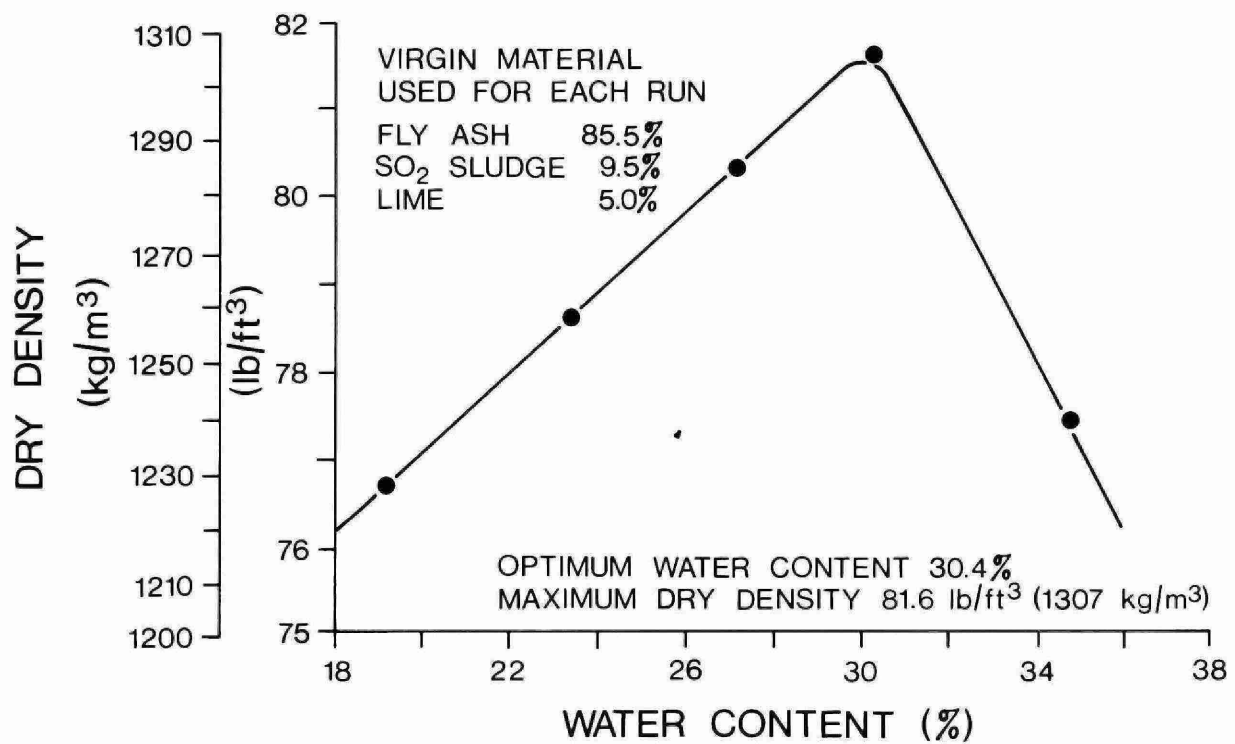


FIG. 4: STANDARD PROCTOR COMPACTION
TEST ON A LIME/FLY ASH/SO₂
SLUDGE MIXTURE

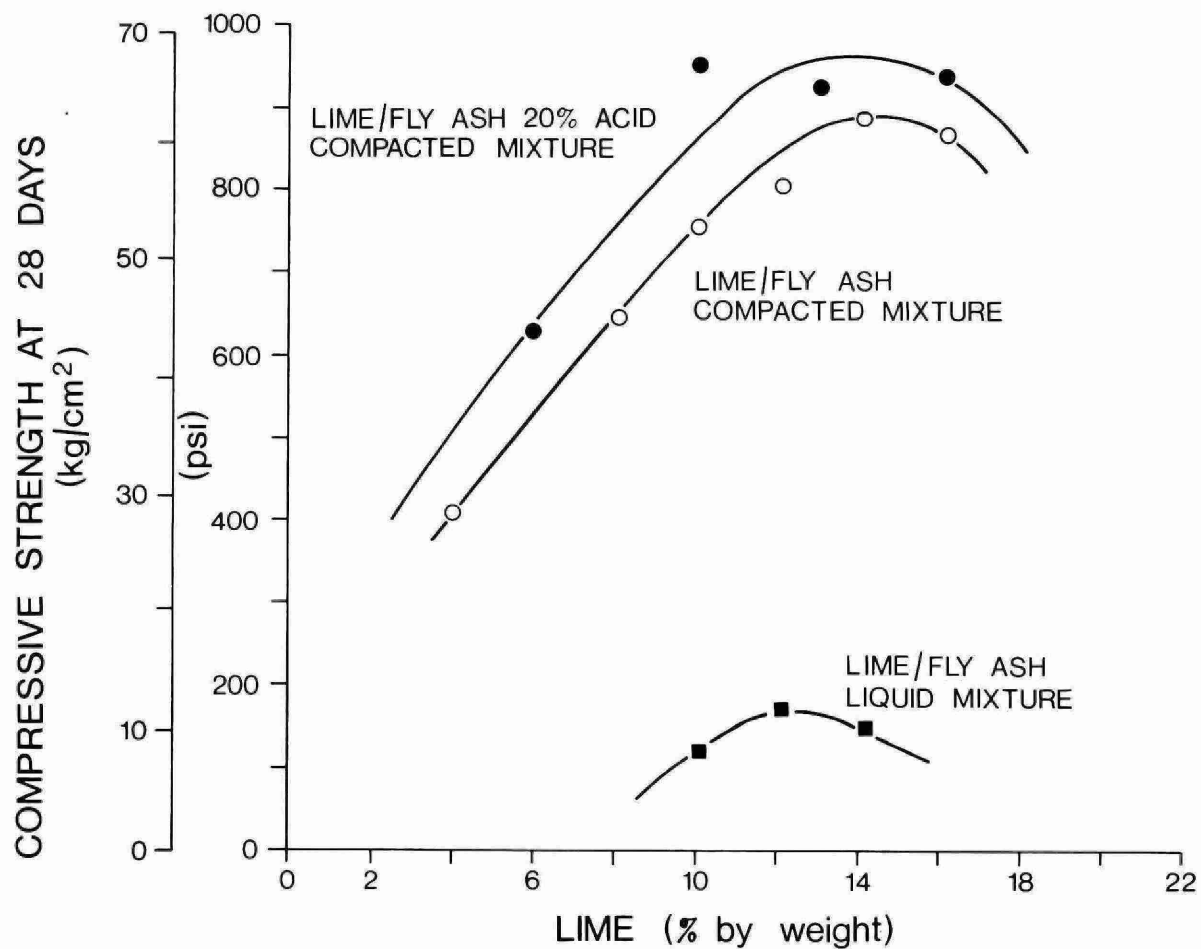


FIG 5: EFFECT OF LIME CONTENT ON COMPRESSIVE STRENGTH OF COMPACTED AND LIQUID MIXTURES

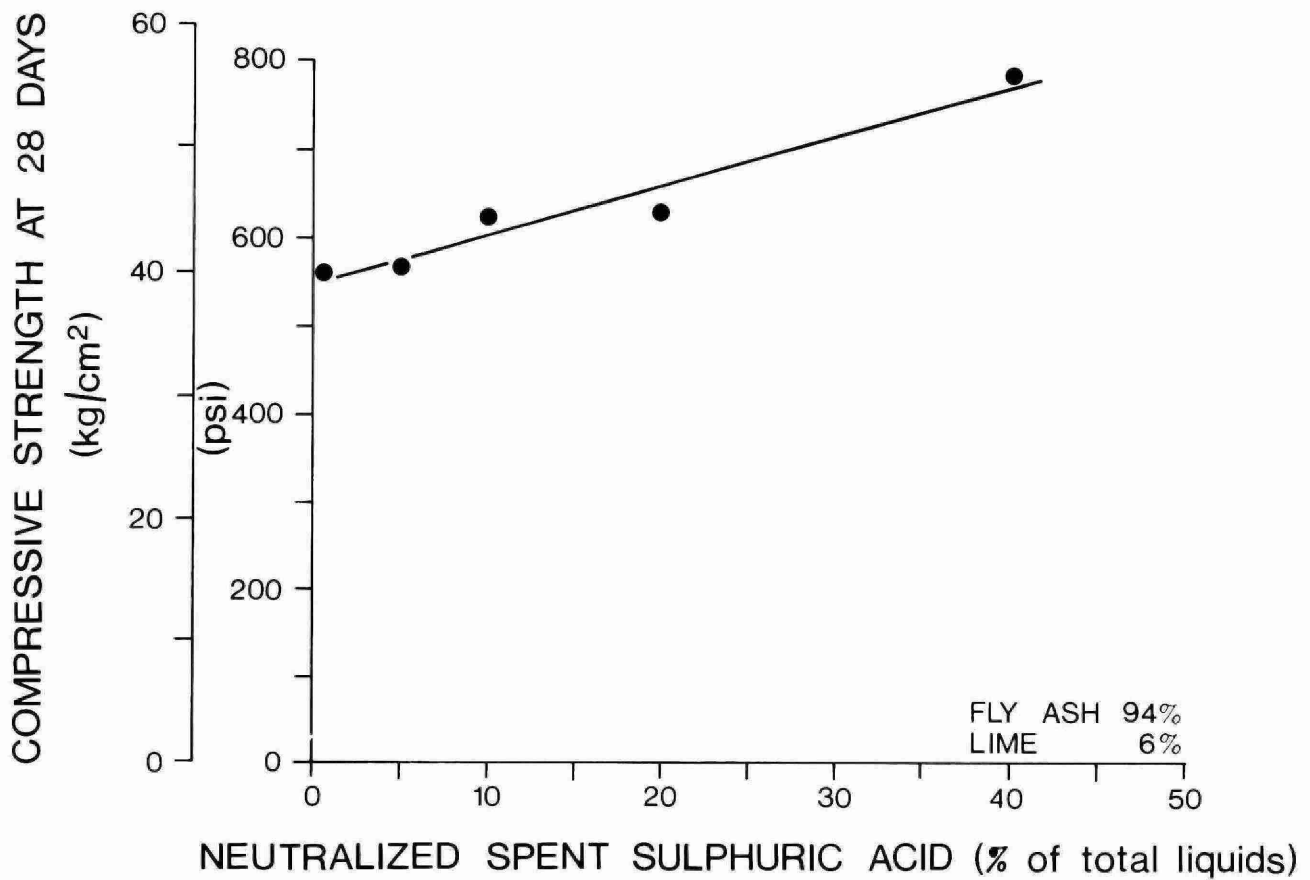


FIG. 6: EFFECT OF ACID CONTENT ON COMPRESSIVE STRENGTH AT A CONSTANT LIME/FLY ASH CONTENT

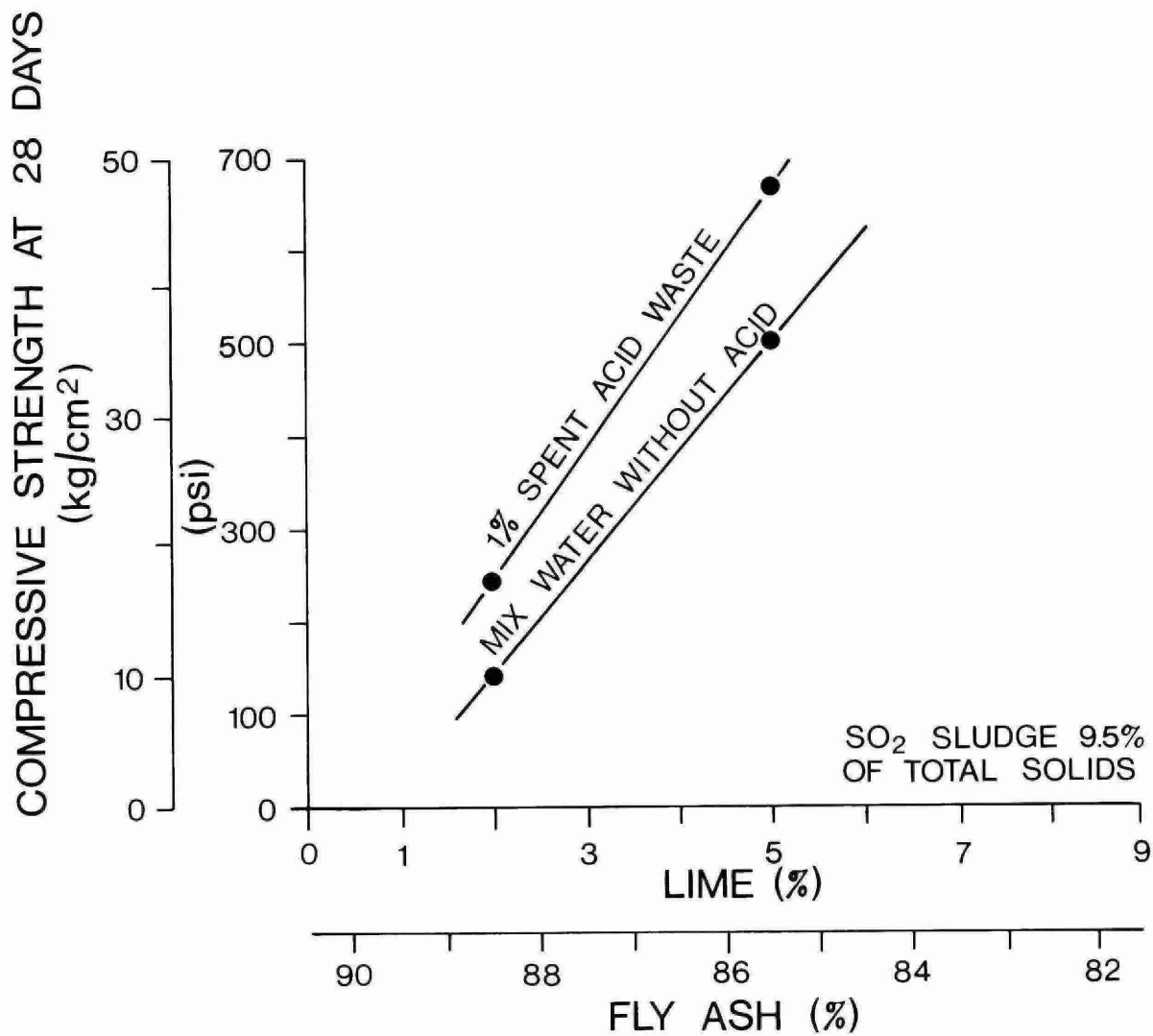


FIG. 7: EFFECT OF SPENT ACID ON COMPRESSION STRENGTH OF A LIME/FLY ASH/SO₂ SLUDGE MIXTURE

Another series of mixes was prepared to check the effect of neutralized, spent sulphuric acid waste on the lime/fly ash/SO₂ sludge mixtures in which the lime/fly ash ratio was varied. The results (Figure 7) demonstrated that the addition of 1% neutralized, spent sulphuric acid solution to a mixture containing 5% lime, 85.5% fly ash and 9.5% SO₂ sludge increased the compressive strength by 165 pounds per square inch compared to a mixture without acid.

5.3.4 Effect of SO₂ sludge

A series of mixes was tested in which a portion of the fly ash was replaced with SO₂ sludge. The proportion of SO₂ sludge to fly ash was varied from 1:3 to 1:30 parts by weight. The results (Figure 8) indicated that the compressive strength of the mixture increased to a maximum (550 psi) at 5% SO₂ sludge, after which further sludge additions produced declining compressive strengths.

5.4 Phosphate-Bearing Sewage Sludge

5.4.1 Choice of a basic matrix

A basic matrix was selected for compressive strength and leaching studies consisting of:

- Fly Ash 90.2% by weight of total solids
- Lime 5.0% by weight of total solids
- SO₂ Sludge 4.8% by weight of total solids
- Neutralized, Spent 1.0% by weight of total liquids
Sulphuric Acid at a concentration of 3.4% H₂SO₄.

5.4.2 Effect of sewage sludge on compressive strength

A series of mixes were prepared in which an increasing quantity of sewage sludge was added to the basic matrix. The sewage sludge was added to the mix in the dry state in proportions varying from 0 to 6.25% of dry weight total solids. The effect of sewage sludge addition on the compressive strength of the basic matrix is shown in Figure 9. The compressive strength decreased, but did not decline below 400 psi with increasing quantities of sewage sludge.

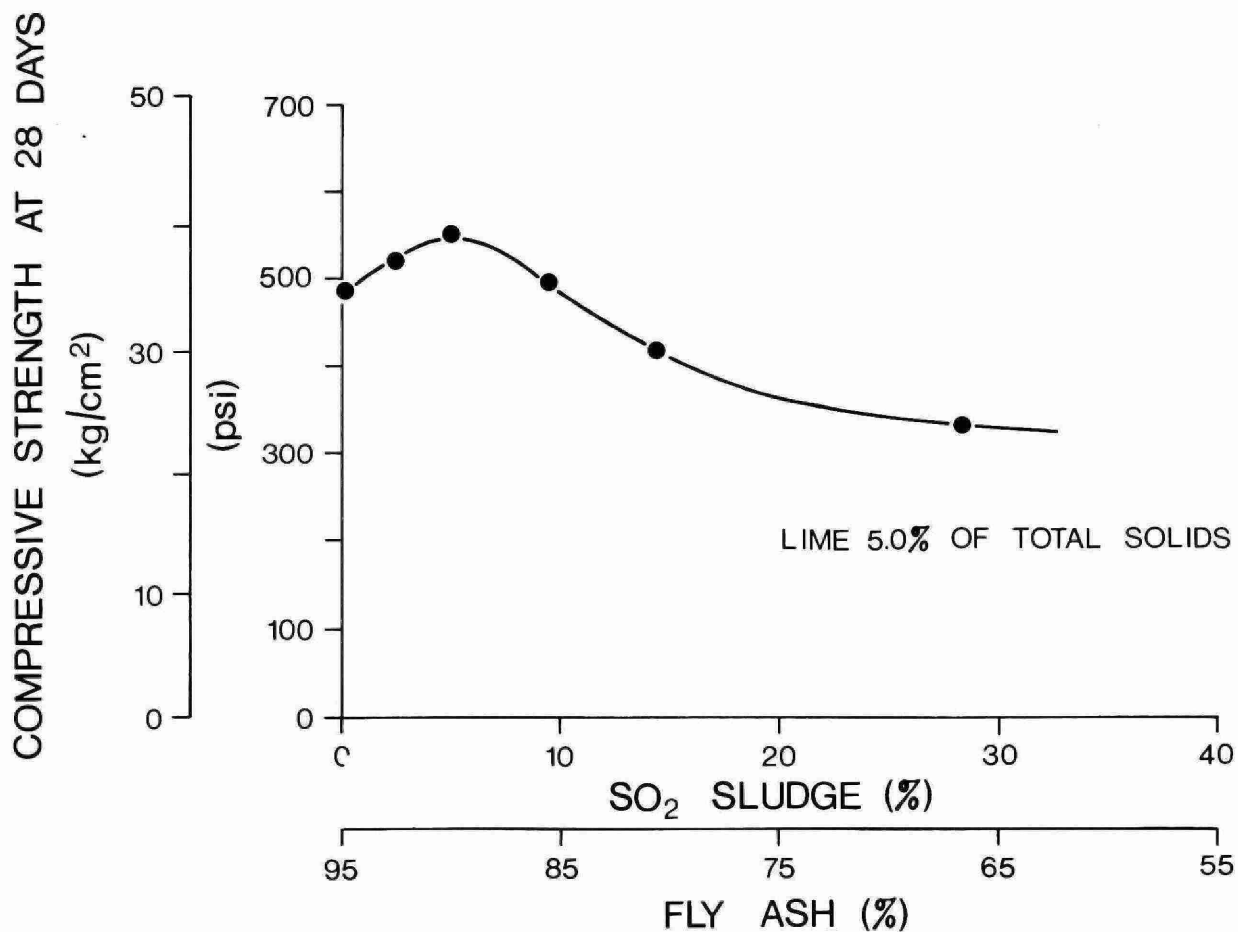


FIG. 8: EFFECT OF SO₂ SLUDGE ON COMPRESSION STRENGTH OF LIME/FLY ASH/SO₂ SLUDGE MIXTURE

COMPRESSIVE STRENGTH AT 28 DAYS

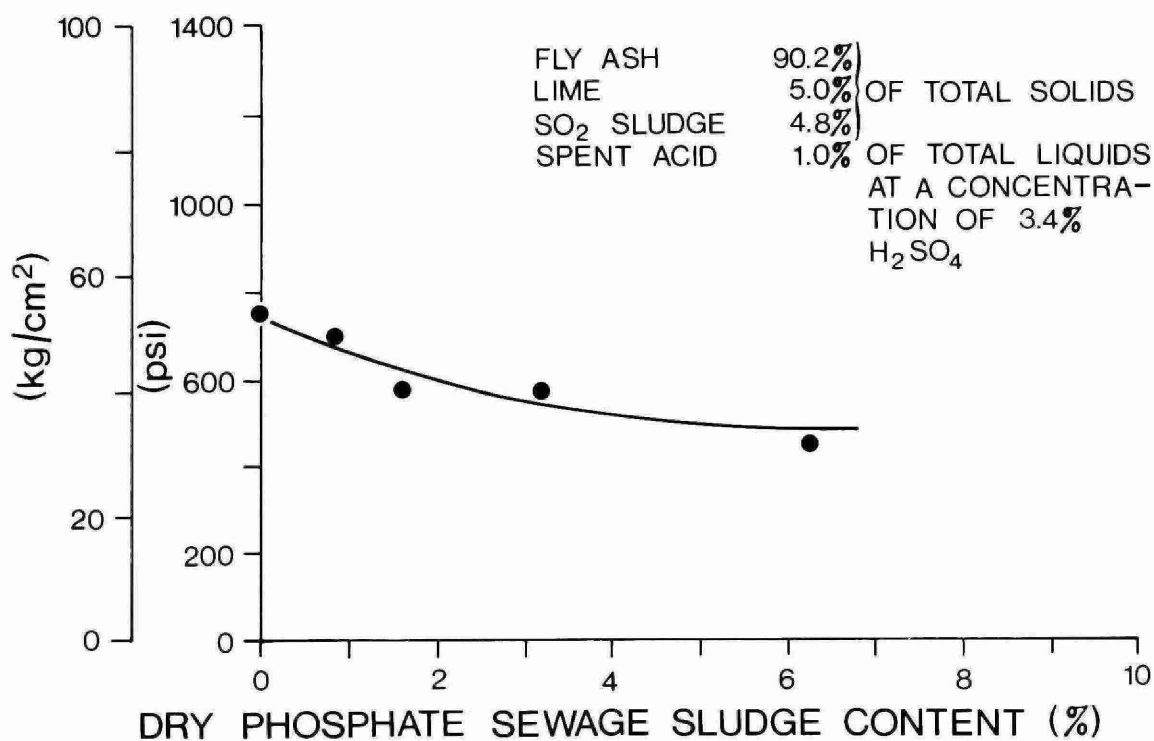


FIG. 9: EFFECT OF SEWAGE SLUDGE CONTENT ON COMPRESSIVE STRENGTH OF THE BASIC MATRIX

5.4.3 The ability of mixes to retain phosphates

Leaching experiments were performed with duplicates of specimens which had been tested for compressive strength. Each specimen was placed in 250 ml of distilled water and agitated. Leachate was analysed after one, three, seven and fifteen days for total phosphate. The amount of phosphate leached was minimal (<0.01% of total PO_4 input) and did not increase with increasing amounts of phosphate-bearing sewage sludge (Table 5). Although these results are encouraging, longer leaching periods (of the order of one year) should be examined in order to better assess the likelihood of phosphate re-entry into groundwater from cemented sludges.

TABLE 5. LEACHING OF TOTAL PHOSPHATE FROM COMPACTED MIXTURES

Test No.	Total PO_4 (mg)		Total PO_4 Leached as % of Input
	Input	Leachate*	
26	421.68	0.04	0.0095
27	478.12	0.01	0.0021
28	580.47	<0.01	<0.0020
29	783.13	0.04	0.0051

*After 15 days cumulative leaching.

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